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14. ABSTRACT

The purpose of this project was to develop new numerical methods for the study of the expected behavior of stochastic simulations (such as kinetic Monte Carlo, kMC, or Brownian Dynamics, ED) as well as problems involving complex media (i.e. homogenization, or effective medium theory). Many situations arise in current engineering modeling where stochastic simulators are available, yet closed equations for the expected behavior are not explicitly known. Our coarse time-stepper based approach is a bridge that connects microscopic/detailed simulation with macroscopic, systems level numei-ical analysis, enabling tasks like prediction, stability analysis, controller design and optimization to be performed directly on the microscopic models. We have constructed bridges between existing and future microscopic simulation codes (kMC, MD, MC, BD, LB etc.) and traditional, continuum numerical analysis. We trade function evaluations (in the continuum computations) for appropriately initialized "bursts" of microscopic simulations, executed over short space and time intervals, followed by post-processing based on system-identification techniques.

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EXPECTED DYNAMICS in COMPLEX MEDIA & STOCHASTIC SIMULATIONS: A COARSE-TIMESTEPPER-BASED APPROACH

F49620-02-1-0397

Final Technical Report

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Abstract

The purpose of this project was to develop new numerical methods for the study of the expected behavior of stochastic simulations (such as kinetic Monte Carlo, kMC, or Brownian Dynamics, BD) as well as problems involving complex media (i.e. homogenization, or effective medium theory). Many situations arise in current engineering modeling where stochastic simulators are available, yet closed equations for the expected behavior are not explicitly known. Our coarse time-stepper based approach is a bridge that connects microscopic/detailed simulation with macroscopic, systems level numerical analysis, enabling tasks like prediction, stability analysis, controller design and optimization to be performed directly on the microscopic models. We have constructed bridges between existing and future microscopic simulation codes (kMC, MD, MC, BD, LB etc.) and traditional, continuum numerical analysis. We trade function evaluations (in the continuum computations) for appropriately initialized "bursts" of microscopic simulations, executed over short space and time intervals, followed by post-processing based on system-identification techniques. Separation of time scales is another important ingredient of the bridge between micro-simulation and macro-modeling.

Objectives

We want to enable advanced, computer-assisted analysis and design computations for complex, nonlinear, distributed (spatially varying) processes described by microscopic (atomistic, stochastic, agent-based) models. We construct a bridge that allows scientific computing tasks (like simulation, stability and bifurcation analysis, control and optimization) to be performed for problems for which the physical description is available at a "fine" microscopic or stochastic level, but the questions asked are at a macroscopic, systems level. This bridge takes the form of software "wrappers", that can be combined with state of the art microscopic simulation codes (like kinetic Monte Carlo, kMC, equilibrium MC, Brownian Dynamics, BD, or general agent-based, AB) simulators. We can also work with evolution equations in complex/random media (i.e., effective medium theory), discrete media (e.g. lattice dynamics), and, fortuitously, with large scale legacy codes, which can also be enabled by these "wrappers". Systems theory

tools (system identification, separation of time scales) are vital in this computational enabling technology.

Accomplishments

We have been able to accelerate the simulation, as well as the stability and bifurcation analysis, and in some cases the optimization and control of several stochastic problems. **(a)** We demonstrated how to use coarse timesteppers to control stochastic simulations in our *AIChE J.* paper last July. Using coarse timesteppers to locate unstable stationary states of the expectation of the kMC simulations of surface reactions, we were then able to estimate the action of the slow coarse Jacobian using matrix-free methods, and used it to design a macroscopic stabilizing controller. **(b)** Our work on the coarse time-stepper based analysis of Brownian Dynamics problems appeared in *J. Chem. Phys.* last June; we were able to compute the bifurcation behavior of the orientation statistics of nematic liquid crystals by acting directly on the Brownian Dynamics simulator. **(c)** Two publications are in the final steps of completion from a collaboration with Prof. A. Z. Panagiotopoulos and Dr. Dima Kopelevich on the coarse computation of equilibrium Monte Carlo simulations, in particular the acceleration of grand canonical Monte Carlo simulations of micelle aggregation. **(d)** A paper on the acceleration of kMC simulations of dislocation dynamics was recently submitted to *Phys. Rev. Letters* in collaboration with Prof. D. Srolovitz and Dr. Mikko Haataja. **(e)** We have started a collaboration with Prof. G. Karniadakis and Dr. Dongbin Xiu at Brown, on combining the "polynomial chaos" theory (Spanos and Ghanem) with our coarse computations. In addition, we have also started a collaboration with Prof. Ghanem and his student You along these lines on the coarse computation of passive scalar transport. We started working with Prof. J. Rawlings of the U. of Wisconsin on coarse model predictive control, as well as with Profs. Stuart and Barkley of the U. of Warwick on coarse optimization. **(f)** With Prof. S. Levin at Princeton, Prof. Gear and Dr. Cisternas, we were able to accelerate computations in evolutionary epidemiology (agent based models of evolving diseases and of influenza A in particular. A paper from this work was recently submitted to *Proc. Roy. Soc. London* and one more paper will be submitted shortly to *Proc. Natl. Acad. Sci. USA*. **(g)** With Dr. Siettos and Prof. Maroudas from Umass we have a paper in press in *Int. J. Bif. Chaos* on augmented ensembles for the computation of unstable branches of stochastic simulators. **(h)** With Drs. Runborg and Moeller at KTH in Sweden we have submitted a paper to *Nonlinearity* on the computation of the effective behavior of discrete media (which has applications to neuron lattices). **(i)** With Dr. Xiu (last year from Brown and now from Los Alamos) we have started working towards the study of diffusion in random media as a fundamental example of the coarse timestepping and patch dynamics applied to problems depending on random variables. **(k)** With Dr. S.-J. Moon we have been studying the dynamics of ensembles of coupled oscillators; a paper from this work will be soon submitted to *Phys. Rev. Letters.* The collaboration (with the Fritz-Haber Institut in Berlin) on addressable catalytic media (as examples of complex media) had 2 Phys. Rev. Letters, a review paper in J. Catalysis as well as a Science article this summer. A collaboration started with Los Alamos National Laboratory towards particle-based filtering (coarse integration of Fokker-Planck equations based on which estimation and prediction are made). Collaborations with Professors Yip (MIT) and Li (Ohio State) on

computational materials science led to a Proceedings publication and will continue; with Profs. Tannenbaum and Ben Arous on particle-based algorithms for image processing another collaboration just started. We should also mention **(l)** our work on accelerating chemotactic computations with Drs. Setayeshgar and Siettos, and Profs. Othmer and Gear, which was submitted for publication to SIAM MMS late this summer.

In summary, several examples were successfully tackled and extensive experience was acquired in the acceleration of systems level analysis based on microscopic/stochastic codes. Many of these attempts are now becoming individual research programs. The collaboration with Umass on computational materials science issues will also continue.

Acknowledgement/Disclaimer
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Personnel Supported
Prof. Ioannis G. Kevrekidis, the PI, was partially supported in the summer of 2003. the post-doctoral research associate supported was Dr. Ligang Chen. Graduate students partially supported were Ms. (now Dr.) X. Li, Mr. C. Calderon (2^{nd} year), and Mr. L. Qiao (2^{nd} year).
There was a subcontract with the University of Massachusetts at Amherst (Prof. D. Maroudas as co-PI) that is detailed in the attached report.

Interactions
Seminars by Prof. Kevrekidis: Several seminars at Universities (6) and National Labs (2), several invited/plenary talks (6) and presentations at conferences (15); Visits and discussions with UTRC personnel involved Dr. C. Jacobson and Dr. M. Myers (complex system modeling techniques, model reduction in computational chemistry).

Honors/Awards **(a)** J. D. Crawford Prize, 2003, Society of Industrial and Applied Mathematics, for the multiscale computational framework that constitutes the effort described in this proposal. **(b)** plenary talks: e.g. NSF-Sponsored Mediterranean ChE meeting in Greece, May 2003; SIAM Dynamical Systems Meeting in Utah, May 2003; Non-Equilibrium Thermodynamics & Complex Fluids Meeting, Princeton, August 2003; Biocomplexity V, Notre Dame, August 2003; PATT03 meeting in Dresden, August 2003; Invariant Manifold meeting in Zuerich, August 2003.

Publications

1. ``Coarse Brownian dynamics for nematic liquid crystals: Bifurcation, projective integration and control via stochastic simulation" C. Siettos, M. D. Graham and I. G. Kevrekidis, J. Chem. Phys.118(22) pp.10149-10157 (2003)

2. ``Microscopic/Stochastic timesteppers and Coarse Control: a kinetic Monte Carlo example", C. I. Siettos, A. Armaou, A. G. Makeev and I. G. Kevrekidis AIChE J., appeared July 2003
3. ``Coarse Bifurcation Diagrams via Microscopic Simulators: a State-Feedback Control-Based Approach", C. I. Siettos, D. Maroudas and I. G. Kevrekidis, *Int.J.Bif. Chaos,* in press (2004)
4. ``Wave Initiation through Spatiotemporally Controllable Perturbations", J. Wolff, A. G. Papathanasiou, H. H. Rotermund, G. Ertl, M. A. Katsoulakis, X. Li and I.G.K., Phys. Rev. Lett.,90(14) 148301(4) (2003).
5. ``Local manipulation of catalytic surface reactivity", J. Wolff, A. G. Papathanasiou, H. H. Rotermund, G. Ertl, X. Li and I. G. K., J. Catal., 216 pp.246-256 (2003)
6. Deciding the Nature of the Coarse Equation through Microscopic Simulation: an Augmented Lagrangian Approach", SIAM MMS, J. Li, P. G. Kevrekidis, C.W. Gear and I.G.K., appeared September 2003
7. ``Heartbeats of an ultra thin catalyst", F. Cirak, J. E. Cisternas, A. M. Cuitino, G. Ertl, P. Holmes, I.G.K., M.Ortiz, H. H. Rotermund, M. Schunack and J. Wolff, Science, appeared June 2003.
8. ``Time-steppers and coarse control of microscopic distributed processes", A. Armaou, C. I. Siettos and I. G. Kevrekidis, Int. J. Robust and Nonlinear Control, in press.
9. ``Equation-free multiscale computation: enabling microscopic simulators to perform system-level tasks", with C. W. Gear, J. M. Hyman, P. G. Kevrekidis, O. Runborg and K. Theodoropoulos, *Comm. Math. Sciences* **1**(4) pp.715-762 (2003); original version can be obtained as physics/0209043 at arXiv.org.
10. Effective equations for discrete systems: A time stepper based approach", J. Moeller, O. Runborg, P. G. Kevrekidis, K. Lust and I.G.K., to Nonlinearity, July 2003; can be found as physics/0307153 at arXiv.org.
11. ``Application of Coarse Integration to Bacterial Chemotaxis" S. Setayeshgar, C. W. Gear, H. G. Othmer and I. G. K., to {\it SIAM MMS}. August 2003; can be found as physics/0308040 at arXiv.org
12. ``Equation-free modeling of evolving diseases: coarse-grained computations with individual-based models", J. Cisternas, C. W. Gear, S. Levin and I.G.K., to Proc. Roy. Soc. London, Sept. 2003; can be found as nlin.AO/0310011 at arXiv.org.
13. Apparent hysteresis in a driven system with self-organized drag", M. Haataja, D. Srolovitz and I.G.K., to *Phys. Rev. Lett.,* October 2003; can be found as cond-mat/0310460 at arXiv.org.
14. Equation-Free multiscale computations for a lattice-gas model: coarse-grained bifurcation analysis of the NO+CO reaction on Pt(100)", A. G. Makeev and I.G.K., *Chem. Eng. Sci.,* in press, 2004.
15. ``Parrinello-Rahman Dynamics for Vortex Lattices", R. Carretero-Gonzalez, P. G. Kevrekidis, I.G.K., D. Maroudas, D. J. Frantzeskakis, to {\it Phys. Rev. Lett.}, September 2003.
16. Damping Factors for the gap-tooth scheme, G. Samaey, I.G.K. and D. Roose, Proceedings of the 2003 Multiscale Summer School in Lugano, to be published by Springer, October 2003; also physics/0310014 at arXiv.org

17. Nonlinear Dynamics Analysis through Molecular Dynamics Simulations, I. G. Kevrekidis, J. Li and S. Yip, Proceedings of the 2003 Multiscale Summer School in Lugano, to be published by Springer, October 2003
18. Exploration of Coarse Free Energy Surfaces templated on continuum numerical methods, D. Passerone and I. G. Kevrekidis, Proceedings of the 2003 Multiscale Summer School in Lugano, to be published by Springer, October 2003

University of Massachusetts TECHNICAL REPORT

RESEARCH ACTIVITIES

Research activities at U. Mass. were centered around two main themes: (i) development of stochastic and deterministic descriptions of microscopic dynamics with emphasis on kinetic Monte Carlo (KMC) and finite-temperature molecular-dynamics (MD) simulations and (ii) applications of these simulations toward expected-dynamics studies following the coarse-time-stepper-based approach developed by Prof. Kevrekidis and his research group at Princeton University. In the case of KMC simulation, we focused on lattice Monte Carlo descriptions of surface transport and reaction processes and worked closely with the Princeton group. Future work also will include simulations of thin-film and nanostructure growth through hybrid off-lattice KMC schemes that we are currently developing at U.Mass. In the case of MD simulation, we developed coarse finite-temperature MD tools for model bulk systems with interatomic interactions described by simple Lennard-Jones (pair) potentials; in addition, we addressed a suite of materials mechanics problems in metallic systems with interatomic interactions described either by simple Morse (pair) potentials or more sophisticated embedded-atom method (many-body) potentials. We have developed canonical (isostrain-isothermal) MD simulators for the model bulk systems and both canonical and isostress-isothermal MD simulators for the crystalline metallic systems that we studied.

Our coarse KMC simulations place emphasis on accelerating KMC dynamics using projective integration methods developed by Kevrekidis & Gear and on conducting systematic bifurcation analyses for "spatially distributed" surface systems under conditions where the rates of reaction and diffusion are comparable. Similarly, our coarse MD simulations emphasize on developing accelerated MD schemes based on projective integration algorithms and on enabling MD-based bifurcation analyses in a manner analogous to our demonstrated coarse KMC-based system-level studies. Our ultimate goal is to enable accelerated-MD-based system-level analysis for applications over a broad range of problems from surface physical chemistry to hard materials mechanics. Much of this work is currently in progress; we anticipate that our results will appear in a substantial number of high-quality publications (also see Publications section below). Specifically, we are in the process of implementing our coarse MD tools to carry out an ambitious, comprehensive parametric study of deformation and failure of ductile bulk metals and metallic thin films; operating parameters include: loading mode, applied strain rate, final applied strain, temperature, and thin-film thickness. Preliminary results have not only contributed to development of response diagrams but also revealed new atomic-scale void growth and material failure mechanisms.

Furthermore, theoretical work at U.Mass. has focused on developing an "alternative" augmented Lagrangian formulation of deterministic atomic-scale dynamics aiming at predictions of expected coarse behavior. This formulation allows for MD simulations within an augmented-space representation that incorporates directly into the dynamical description the coarse bifurcation parameter(s); therefore, coarse bifurcation analysis can be implemented as an integral part of the augmented "fine" (MD) time stepper. Theoretical development of this alternative methodology is currently reaching completion and computational implementation will soon follow with applications to the materials mechanics problems discussed above.

SPECIFIC RESEARCH TASKS EXECUTED

- Development of computer codes implementing the coarse-time-stepper-based methodology around KMC simulators. Capabilities include: (i) coarse projective KMC simulation for time-stepping acceleration, (ii) coarse bifurcation and stability analysis based on KMC simulation, and (iii) state-feedback control-based approach for coarse bifurcation analysis via KMC simulation;
- Application of the above tools utilizing KMC simulators to study coupled surface reaction and diffusion processes on catalytic surfaces;

- Development of computer codes implementing the coarse-time-stepper-based methodology around canonical (isostrain-isothermal) and isostress-isothermal MD simulators at finite temperature. Capabilities include: (i) coarse projective MD simulation that improves the severe time-scale limitations of MD and (ii) coarse bifurcation and stability analysis via MD simulation;
- Application of the above tools utilizing MD simulators to study: (a) equilibrium behavior of crystalline and disordered phases of bulk materials, (b) vacancy clustering and void formation in crystalline solids supersaturated in vacancies, (c) structural response of crystalline solids to applied mechanical loading, including fracture and structural transition, and (d) ductile void growth & failure in bulk metals & metallic thin films; and
- Augmented Lagrangian formulation for MD-based system-level analysis. Computational implementation will utilize the MD simulators developed in this project.

PEOPLE SUPPORTED at the University of Massachusetts

Funds from this AFOSR grant provided partial support for the U.Mass. PI (Prof. D. Maroudas) and one of his graduate students, Miguel A. Amat, who has been conducting research on the general subject of this project toward his Ph.D. degree in Chemical Engineering. The graduate student was supported for one semester (stipend, benefits, curriculum fee) and the PI was supported for two summer months.

PUBLICATIONS acknowledging AFOSR support

1. C. I. Siettos, D. Maroudas, and I. G. Kevrekidis, "Coarse Bifurcation Diagrams via Microscopic Simulators: A State-Feedback Control-Based Approach," *Mediterranean IEEE Control Conference Proceedings*, in press (2003).
2. C. I. Siettos, D. Maroudas, and I. G. Kevrekidis, "Coarse Bifurcation Diagrams via Microscopic Simulators: A State-Feedback Control-Based Approach," *International Journal of Bifurcations and Chaos*, in press (2004).
3. F. Milstein, J. Zhao, and D. Maroudas, "Atomic Pattern Formation at the Onset of Stress-Induced Elastic Instability: Fracture or Phase Change?" manuscript in final stage of preparation for submission to *Physical Review E*.
4. J. Li, S. Yip, F. Milstein, I. G. Kevrekidis, and D. Maroudas, "Numerical Bifurcation Analysis Based on Molecular-Statics Simulation: A Systematic Method for Analysis of Mechanical Stability and Stress-Induced Structural Transitions in Crystals," manuscript in preparation for submission to *Journal of Chemical Physics*.
5. M. A. Amat, C. I. Siettos, I. G. Kevrekidis, and D. Maroudas, "Coarse Bifurcation Analysis of Surface Reaction and Diffusion Processes Modeled by Kinetic Monte Carlo Simulation," manuscript in preparation.
6. M. A. Amat, I. G. Kevrekidis, and D. Maroudas, "Coarse Projective Kinetic Monte Carlo Simulation of Surface Reaction and Diffusion Processes," manuscript in preparation.
7. M. A. Amat, I. G. Kevrekidis, and D. Maroudas, "Coarse Projective Canonical Molecular-Dynamics Simulation of Crystalline and Disordered Phases of Bulk Materials," manuscript in preparation.
8. M. A. Amat, I. G. Kevrekidis, and D. Maroudas, "Analysis of Vacancy Clustering and Void Formation in Crystalline Solids Using Coarse Projective Canonical Molecular-Dynamics Simulation," manuscript in preparation.
9. K. Kolluri, M. A. Amat, M. R. Gungor, I. G. Kevrekidis, and D. Maroudas, "Ductile Void Growth in Metallic Thin Films: Strain Rate Effects Analyzed by Coarse Projective Molecular-Dynamics Simulation," manuscript in preparation.
10. J. Zhao, M. R. Gungor, F. Milstein, I. G. Kevrekidis, and D. Maroudas, "Coarse Bifurcation Analysis of Isostress Molecular-Dynamics Simulations: Response of Crystalline Solids to External Mechanical Stress," manuscript in preparation.

A substantial body of work that is currently in progress will result in many more publications that will acknowledge the AFOSR support. This work focuses on two main themes: (i) improvement of the time-scale limitations of deterministic & stochastic microscopic simulators using coarse projective integration methods and (ii) coarse bifurcation analysis of molecular-dynamics simulations.

TECHNICAL PRESENTATIONS acknowledging AFOSR support

1. D. Maroudas, "Multiscale Modeling," United Technologies Research Center, March 2003, E. Hartford, Connecticut **(Invited Talk)**.
2. D. Maroudas, "Multiscale Modeling of Complex Systems: Status, Challenges, and Opportunities," Process Systems Engineering Consortium, University of Massachusetts, Amherst, June 2003 **(Invited Talk)**.
3. D. Maroudas, "Recent Contributions of Molecular Simulation to the Modeling of Electronic Materials Processing and Reliability," Foundations of Molecular Modeling and Simulation (FOMMS) 2003 Meeting, July 2003, Keystone, Colorado **(Invited Talk)**.
4. D. Maroudas, "Analysis of Electromechanically-Induced Failure of Metallic Thin Films Mediated by Void Dynamics," Workshop on Aging and Long-Term Reliability of Microelectronics Materials and Devices, Vanderbilt University, October 2003, Nashville, Tennessee **(Invited Talk)**.
5. D. Maroudas, "Multiscale Modeling: Status and Opportunities in Research and Education," CAST Division Plenary Talk, AIChE Annual Meeting, November 2003, San Francisco, California **(Invited Plenary Talk)**.
6. D. Maroudas, "Multiscale Modeling of Materials Processing and Function," Session on Multiscale Systems Simulation and Control, American Control Conference, June 2004, Boston, Massachusetts **(Invited Talk)**.
7. D. Maroudas, J. Li, S. Yip, F. Milstein, and I. G. Kevrekidis, "Numerical Bifurcation Analysis Using Deterministic Atomistic Simulation: Instabilities and Structural Transitions in Crystals," AIChE Annual Meeting, November 2002, Indianapolis, Indiana.
8. A. G. Makeev, D. Maroudas, A. Z. Panagiotopoulos, and I. G. Kevrekidis, "Coarse Bifurcation Analysis of Kinetic Monte Carlo Simulation Results," AIChE Annual Meeting, November 2002, Indianapolis, Indiana.
9. J. Li, D. Maroudas, I. G. Kevrekidis, and S. Yip, "Coupling Coarse Variables to Microscopic Simulations," AIChE Annual Meeting, November 2002, Indianapolis, Indiana.
10. J. Zhao, F. Milstein, and D. Maroudas, "Molecular-Dynamics Analysis of Nonlinear Elastic Instability, Structural Transition, and Failure in Crystals Under Stress," AIChE Annual Meeting, November 2003, San Francisco, California.
11. C. I. Siettos, C. W. Gear, D. Maroudas, and I. G. Kevrekidis, "Enabling Microscopic Models to Perform System-Level Tasks: A Novel Framework for Computer-Aided Multiscale Analysis," AIChE Annual Meeting, November 2003, San Francisco, California.